TRANSESTERIFICATION OF PALM OIL FOR BIODIESEL PRODUCTION USING Ni/CaO SUPPORTED WITH ALUMINA BEADS

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Abstract

Biodiesel has gained interest among researchers as an alternative fuel to replace fossil fuels due to its sustainability. Biodiesel can be produced by transesterification of plant oils with methanol using suitable catalysts. Recently, application of heterogeneous catalyst has attracted considerable interest in biodiesel production compared to homogenous catalyst due to their reproducibility. In this study, biodiesel was produced by transesterification of palm oil with methanol catalyzed by calcium oxide coated on alumina beads and doped with nickel. The objective of this study is to determine the optimum catalyst loading of the transesterification process. The catalyst was prepared by heating a mixture of calcium nitrate, nickel(II) nitrate hexahydrate and alumina beads at 700°C. This temperature was selected after performing a thermogravimetric analysis on the calcium nitrate. In this study, the highest yield of 24.24% was obtained from transesterification reaction at optimum conditions of 5 hour reaction time, 1:25 oil-methanol molar ratio and 65°C of reaction temperature with 4 wt% of catalyst loading. Quantification and identification of biodiesel was done using gas chromatography mass spectrometry (GCMS).

Keyword: Biodiesel, Dopant, Heterogeneous Catalyst, Palm Oil, Transesterification

Introduction

In recent studies, researchers have shown considerable interest in the field of biodiesel. Biodiesel is an alternative for petroleum diesel to overcome the insufficiency of petroleum-based sources. However, the price for this kind of sources is not constant and changeable. Biodiesel is a mixture of methyl esters produced through transesterification of animal fat or vegetable oils. Wong et al. (2015) states that biodiesel is considered as a renewable energy since it originates from biomass. It acts as an alternative fuel for petroleum diesel to reduce the emission of air pollutants and greenhouse gases. By using biodiesel as a vehicle fuel, the environmental quality could be improved. Biodiesel is a mixture of fatty acid methyl esters produced by the catalyzed or uncatalyzed reaction between triacylglycerols (TAGs) or free fatty acids (FFAs) and a short chain alcohol mainly methanol or ethanol (El Sherbiny et al., 2010). Among the advantages of biodiesel are it is a renewable energy, biodegradable, non-toxic, high flash point, good lubricant properties, reduce dependence on imported fuel, as well as free of sulphur.

Palm oil known as an excellent raw material because the biodiesel produced has similar properties to the regular petrodiesel (Zahan et al., 2018). Catalyst can be classified into homogenous and heterogeneous phases (Widayat et al., 2017). The reaction rate of homogenous catalyzed transesterification is high but separation of byproduct glycerine techniques and wastewater treatments are unresolved (Lotero et al., 2005). Enzymatic

catalysis yields high purity of biodiesel at adequate temperature and enables convenient byproduct separation. However, it limits the industrial application due to high-cost of lipase. Homogenous base catalysis is the currently applied technology for biodiesel synthesis. However, the homogeneous catalysts have a major disadvantage in which the catalysts cannot be reused or regenerated.

The separation of homogeneous catalyst from a product is difficult as it involves extra equipment and results in greater cost. Therefore, the problems associated with the homogeneous catalysts can be overcome by implementing heterogeneous catalysts in the reaction. These catalysts are noncorrosive and environmentally friendly in nature. Besides that, they can easily be separated from the products and can be reused with or without regeneration. Therefore, they are preferable as compared to homogeneous catalysts in the production of biodiesel. This also will produce a high-grade glycerol byproduct without expensive refining operations (Di Serio et al., 2007). Heterogeneous catalyst such as CaO catalyst must be held by other compounds such as activated carbon, fly ash or impregnated in a basic solution to increase the percent yield (Hadiyanto et al., 2016). In this study, biodiesel was synthesized by transesterification reaction using calcium oxide supported on alumina beads and doped with nickel (II) nitrate hexahydrate as heterogeneous catalyst. The effect of catalyst loading and methanol to oil molar ratio was investigated.

Materials and Methods

The materials used were palm oil, calcium nitrate tetrahydrate, alumina bead, nickel (II) nitrate hexahydrate, methyl heptadecanoate (as internal standard), standard FAME mixture, 99.9% methanol, n-hexane.

Catalyst Preparation

In this study, calcium nitrate, $Ca(NO_3)_2.4H_2O$ was used as a catalyst of interest and support onto alumina with nickel (II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ as a dopant. The ratio was 1 dopant to 10 bases. The preparation of alumina-$Ca(NO_3)_2$ catalyst and $Ni(NO_3)_2$ is as follows. Each of the metal salts was weighed in a beaker according to the ratio. A 5.82 g of nickel (II) nitrate hexahydrate and 47.23 g of calcium nitrate was dissolved in 100 mL distilled water in a beaker and the solution was mixed and stirred gently by a magnetic stirrer. The mixture was stirred for 30 minutes at room temperature. Then, 30 g of alumina bead support was immersed into catalyst solution for 30 minutes and transferred onto evaporating dish with filter paper on it. After that, the catalyst was transferred into an oven for 24 hours at 80°C for water removal and to permit a good coating of metal on the surface of the supported catalyst. After dried in the oven, the catalysts were analyzed using thermogravimetric analysis (TGA). Later on, calcination in the furnace was performed at 700°C for 5 hours using a ramp of 5°C/min for the elimination of all the metal precursor and excess of water or other impurities. The prepared catalysts were stored in the closed-tight vials and put in desiccator (Sulaiman et al., 2017).

Catalyst Characterization

Thermal decomposition of the Calcium oxide (CaO) was analyzed by thermogravimetric analysis (TGA) using a Perkin Elmer Pyris TGA. The sample was heated from room temperature to 1000°C under air flow with heating rate of 10°C/min (Roschat et al., 2016).

Transesterification with Calcium Nitrate Support Alumina Beads

Transesterification of palm oil was conducted in a 50 mL round bottom flask equipped with a thermometer, a condenser, and a magnetic stirrer. A 10 g of palm oil was mixed with 0.3 g methanol. The solution was stirred for a few minutes to disperse the methanol with the oil.

Then the required amount of catalyst was transferred into the 50 mL round bottom flask containing the reactants. The parameters investigated was catalyst loading (0 wt%, 2 wt.%, 4 wt.%, 6 wt.% and 8 wt.%). The reaction was conducted at 65°C and stirred at 600 rpm for 5 hours.

After the reaction was completed, the reaction mixture was transferred into the test tube and centrifuges for 10 min at 3000 rpm. Two layers were formed and both layers were separated into different vials and the catalyst then was transferred onto filter paper by filtration to remove the alumina beads. The upper layer solution of biodiesel in methanol was mixed with anhydrous sodium sulphate to remove water. The solution was filtered and dried in an oven at 65℃ for 24 hours to remove excess methanol. After 24 hours, the product was weighed and the impure biodiesel yield was calculated (Sulaiman et al., 2017).

Analysis of Gas Chromatography-Mass Spectrometer (GCMS)

Prior to injection, about 0.1 g of biodiesel and 0.01 g internal standard (methyl heptadecanoate) were dissolved in 10 mL n-hexane. This solution was analyzed by gas chromatography using Agilent Technology 7890B Gas Chromatography equipped with MS5977A Mass Spectrometer. The column used was Zebron ZB-FAME (60 m x 0.25 mm x 0.20 μm). The temperature was started at 60°C and was heated at 14 °C/min to 250°C, remain at this temperature for 20 minutes. Identification of FAMEs was done by comparing their retention times with those of authentic standards. Quantification of FAME was done by internal standard method based on the peak area of FAME (Chen et al., 2016). The following equation was used for the calculation of the amount of FAME.

$$C=\frac{(\Sigma A)}{A_{EI}} X \frac{C_{EI} \; X \; V_{EI}}{m} X \; 100\%$$

Where:

ΣA = total peak area of the FAME

A_{EI} = peak area of internal standard

C_{EI} = concentration, in mg/mL, of the internal standard solution

V_{EI} = volume, in mL of the internal standard solution

m = mass, in mg, of the biodiesel sample dissolved in n-hexane

The biodiesel yield was calculated based the following equation

Biodiesel yield = weight of biodiesel / weight of raw oil x 100%

Result and Discussion

Thermogravimetric Analysis

Thermogravimetry is a method to measure the change in weight of a compound as a function of temperature and time (Linggawati et al., 2016). Thermogravimetric analysis (TGA) is carried out to gain the weight loss (TG) and derivative thermogravimetric (DTG) curves in order to achieve optimal calcination temperature for CaO catalyst (Jindapon et al., 2018). In order to explain the effect of calcination temperature, the calcination process of CaO catalyst was investigated with Thermogravimetric analysis (TGA). The result is shown in **Figure 1,** in which decomposition of alumina-CaO catalyst with dopant, Ni $(NO_3)_2.6H_2O$ occured when heated in a controlled environment.

Based on the thermogram obtained, the first cycle shows the percentage of weight loss at temperature range of 33.74℃ to 245.24℃ which was about 7.89%. This was due to the

removal of physically adsorbed water at the catalyst surface. While, the second cycle results in higher percentage of weight loss occurred at temperature range of 318.63°C to 698.48°C which was 75.55% due to the decomposition of the calcium nitrate precursor generated from the reaction. However, the sample weight turned into constant until the temperature reached 700^{0}C. In this case, 700°C may be considered as the suitable calcination temperature for the preparation of the CaO catalyst (Junior et al., 2019).

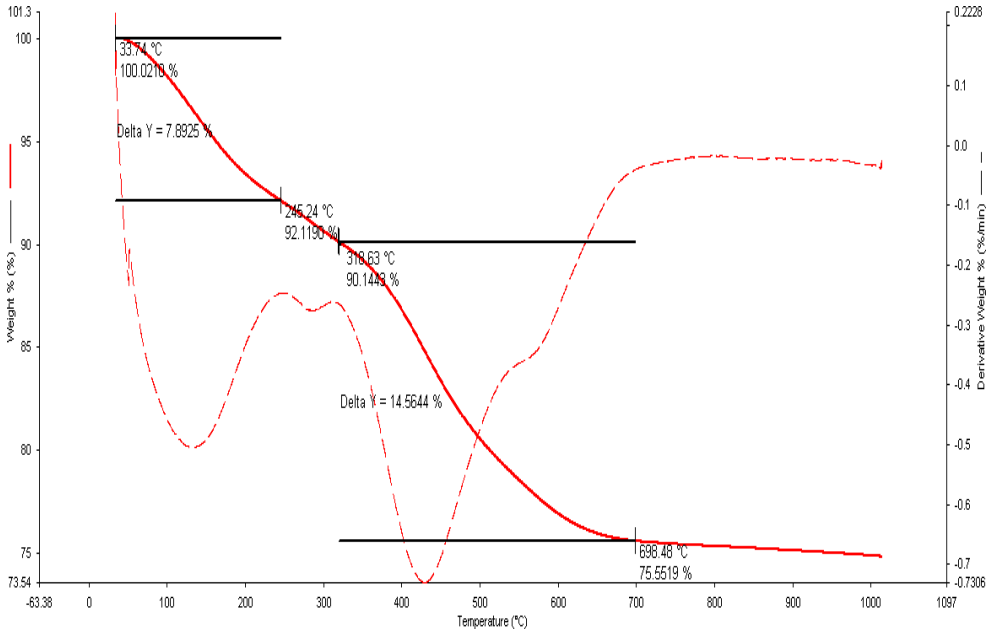

Figure 1 Thermogram of Ni/CaO catalyst

Effect of Catalyst Loading

Figure 2 shows that the low amount of catalyst content, 2 wt% is insufficient to enhance the completion of reaction and the yield of biodiesel was only less than 10% after 5 hours. An addition of 4 wt% of catalyst loading leads to an increase in percentage of methyl ester which is about 24.24%. The sufficient number of active sites available for transesterification reaction of oil attributes to the increase in FAME yield. The excessive amount of catalyst causes the mobility of the reaction mixture to decreased, leads to the poor diffusion between reactants and catalyst which result in decrease of ester content to 17.43% and 15.33% along with increase of catalyst loading to 6 wt% and 8 wt%. (Jitputti et al., 2006; Maneerung et al.,2015).

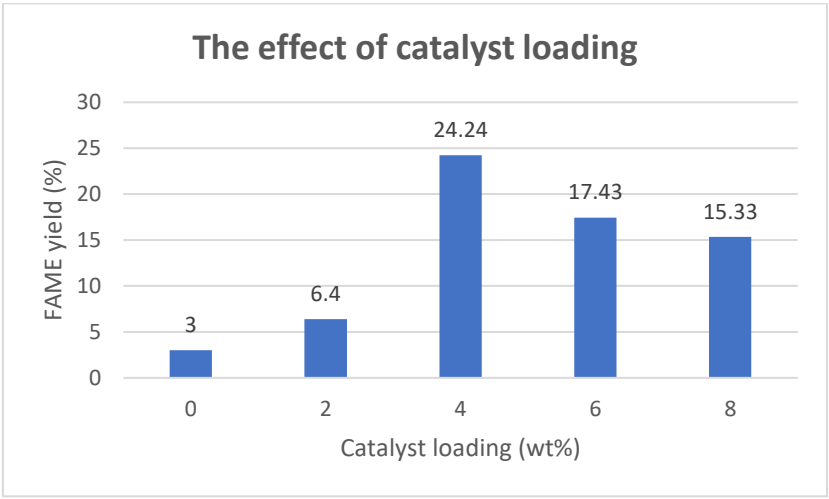

Figure 2 The effect of catalyst loading on the FAME yield

GC Qualitative Analysis

Figure 3 shows the chromatogram of the biodiesel obtained from the reaction. Four peaks of methyl esters were observed, namely methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. The high peaks of methyl palmitate and methyl oleate shows that these methyl esters are the main components of the biodiesel. This agrees with the fatty acid profile of palm oil which is used in this study and thus proves the formation of biodiesel from the oil used. (Ping and Yusof, 2009)

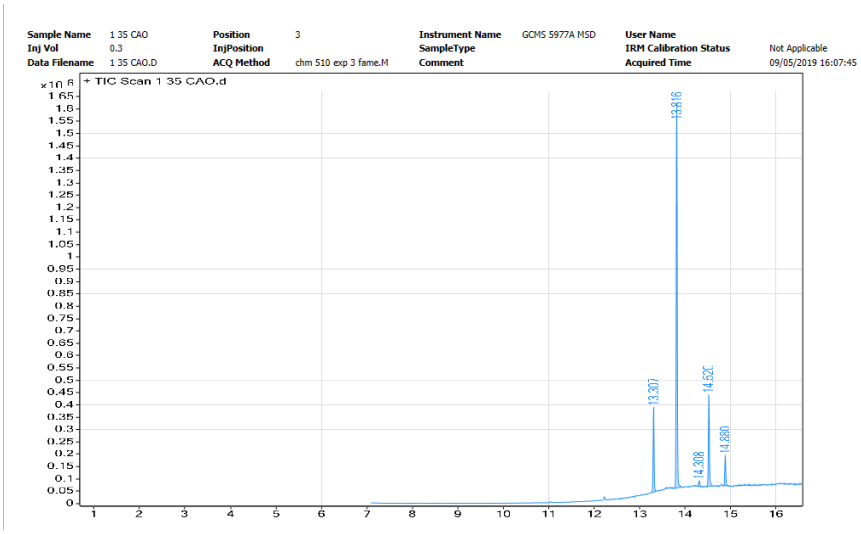

Figure 3 GC-MS chromatogram of biodiesel layer from transesterification reaction

Table 1 shows the presence of methyl esters identified in the biodiesel.

Table 1 The identified FAMEs from the chromatogram of the biodiesel produced by transesterification using 4 wt% catalyst loading

Retention time (min)	Common Name
13.307	Methyl palmitate
13.816	Methyl heptadecanoate (Internal standard)
14.308	Methyl stearate
14.520	Methyl oleate
14.880	Methyl linoleate

Conclusion

In conclusion, the highest FAME yield for transesterification reaction using alumina supported calcium oxide catalyst with nickel dopant was 24.24% with optimum conditions of 5 hour-reaction time, 4 wt.% catalyst loading refluxed at 65°C and 1:25 methanol to oil ratio. The GCMS result confirms the presence of two methyl ester which are methyl palmitate and methyl oleate.

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Conflict of interests

Authors declare no conflict of interest.

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